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(54) Title: PROCESS FOR STABILIZATION OF SILOXANES BY CONTACTING THEM WITH WATER

(57) Abstract: A method for stabilizing silicone dry cleaning solvents that may contain an undesirable acidic impurity capable of causing cyclic siloxane formation, comprising contacting the silicone solvent with an aqueous solution, and separating the silicone solvent.

PROCESS FOR STABILIZATION OF SILOXANES BY CONTACTING THEM WITH WATER

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of US Serial No. 09/466,484, filed December 17, 1999.

TECHNICAL FIELD

The present invention is directed to a process, more specifically, to a process for stabilizing silicone dry cleaning solvents containing acidic impurities.

BACKGROUND

Current dry cleaning technology uses perchloroethylene ("PERC") or petroleum-based materials as the cleaning solvent. PERC suffers from toxicity and odor issues. The petroleum-based products are not as effective as PERC in cleaning garments. Volatile siloxanes are being introduced into the dry cleaning industry as an alternative to PERC. However, there exists a need to stabilize the siloxane solvents to prevent undesirable cyclic siloxane (D₄) formation and polymerization.

Methods for the purification of organopolysiloxanes have previously been reported, but they have not been reported for the purification of certain cyclic siloxanes (D₅). Methods for purifying organopolysiloxanes utilizing elemental metals have been reported (see US 5,245,067). Other patents disclose the purification of polyether silicones by contacting with an aqueous acid and removing the odorous materials formed (see US 5,118,764), or the reaction with hydrogen and a hydrogenation catalyst (see US 5,225,509). Hexamethyldisiloxane has been purified by successive treatments with a condensation catalyst, washing with water, separating the phases, distilling

the siloxane, treating with acid clay and then treating with activated carbon (see US 4,774,346). Siloxanes have also been purified by contacting with steam and distilling out the impurities (see EP 543 665). A deodorization method utilizing active carbon to which a functional group has been fixed through a silanol bond has been reported (see US 5,238,899). Finally, a method was reported for purifying silicone oil by adding a drying agent and an adsorption agent to silicone and passing a low water vapor inert gas through the system (see US 4,661,612).

What is needed in the art is an aqueous extraction system that renders the acidic catalyst inactive, stabilizes the siloxane and suppresses reequilibration and polymerization.

SUMMARY OF THE INVENTION

In a first aspect, the present invention is directed to a method for stabilizing silicone dry cleaning solvents that may contain an undesirable acidic impurity capable of causing cyclic siloxane formation, comprising contacting the silicone solvent with an aqueous solution, and then separating the silicone solvent.

The process of the present invention is effective in preventing formation of certain cyclic siloxanes (i.e., D₄) that are undesirable in the silicone solvent.

As used herein, the terms D₄, D₅ and D₆ refer to cyclic siloxanes having the formula: $-(R_2SiO)_x-$ where x is 4, 5 or 6 (i.e., D₅ is decamethylcyclopentasiloxane).

DETAILED DESCRIPTION OF THE INVENTION

Preferably, the first preferred embodiment of the method of the present invention comprises, contacting a silicone dry cleaning solvent that may contain an undesirable acidic impurity capable of causing cyclic siloxane formation with an aqueous solution, agitating to ensure good mixing of the solvent and the aqueous solution, and separating the silicone solvent.
5 Optionally, a drying agent may be used to dry the solvent. Preferably, the silicone dry cleaning solvent is a volatile linear, branched, cyclic or a combination thereof, siloxane.

Acidic impurities rendered inactive in the present invention are those that typically promote equilibration and redistribution. Examples of acids that promote reequilibration and redistribution include, but are not limited to, LPNC, sulfuric acid, hydrochloric acid, methanesulfonic acid, dodecylbenzenesulfonic acid, p-toluenesulfonic acid, and the like.
10

Solutions suitable as extractants are aqueous solutions of the formula:

15 MeX

wherein Me refers to alkali metals and alkaline earth metals, such as sodium, magnesium, potassium, calcium and the like, and X refers to halogens, such as chlorine, bromine, fluorine and the like, or chalcogen derivatives, such as sulfates, carbonates, bicarbonates, acetates and the like. Examples of suitable solutions include but are not limited to sodium chloride, potassium chloride, sodium bromide, magnesium sulfate and the like. Also suitable as extractants are water and dilute base mixtures such as sodium carbonate and sodium bicarbonate. Mixtures of two or more extractants may also be used.
20 Preferably, the extractant is water.

After extraction, the silicone solvent may be dried with a suitable drying agent. Compounds suitable as the optional drying agent are those
25

that remove the water from the silicone solvent. Examples of suitable drying agents include, for example, 4A molecular sieves, 13X molecular sieves, magnesium sulfate, calcium chloride and calcium sulfate.

Preferably, the silicone dry cleaning solvent is a volatile linear,
5 branched, cyclic or a combination thereof, siloxane.

Compounds suitable as the linear or branched, volatile siloxane solvent of the present invention are those containing a polysiloxane structure that includes from 2 to 20 silicon atoms. Preferably, the linear or branched, volatile siloxanes are relatively volatile materials, having, for example, a
10 boiling of below about 300°C point at a pressure of 760 millimeters of mercury ("mm Hg").

In a preferred embodiment, the linear or branched, volatile siloxane comprises one or more compounds of the structural formula (I):



15 wherein:

M is $R^1_3SiO_{1/2}$;

D is $R^2_2SiO_{2/2}$;

T is $R^3SiO_{3/2}$;

and Q is $SiO_{4/2}$

20 R^1 , R^2 and R^3 are each independently a monovalent hydrocarbon radical; and

x and y are each integers, wherein $0 \leq x \leq 10$ and $0 \leq y \leq 10$ and $0 \leq z \leq 10$.

Suitable monovalent hydrocarbon groups include acyclic hydrocarbon radicals, monovalent alicyclic hydrocarbon radicals, monovalent and aromatic hydrocarbon radicals. Preferred monovalent hydrocarbon radicals are monovalent alkyl radicals, monovalent aryl radicals and monovalent aralkyl radicals.

As used herein, the term "(C₁-C₆)alkyl" means a linear or branched alkyl group containing from 1 to 6 carbons per group, such as, for example, methyl, ethyl, propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, pentyl, hexyl, preferably methyl.

As used herein, the term "aryl" means a monovalent unsaturated hydrocarbon ring system containing one or more aromatic rings per group, which may optionally be substituted on the one or more aromatic rings, preferably with one or more (C₁-C₆)alkyl groups and which, in the case of two or more rings, may be fused rings, including, for example, phenyl, 2,4,6-trimethylphenyl, 2-isopropylmethylphenyl, 1-pentalenyl, naphthyl, anthryl, preferably phenyl.

As used herein, the term "aralkyl" means an aryl derivative of an alkyl group, preferably a (C₂-C₆)alkyl group, wherein the alkyl portion of the aryl derivative may, optionally, be interrupted by an oxygen atom, such as, for example, phenylethyl, phenylpropyl, 2-(1-naphthyl)ethyl, preferably phenylpropyl, phenoxypropyl, biphenyloxypropyl.

In a preferred embodiment, the monovalent hydrocarbon radical is a monovalent (C₁-C₆)alkyl radical, most preferably, methyl.

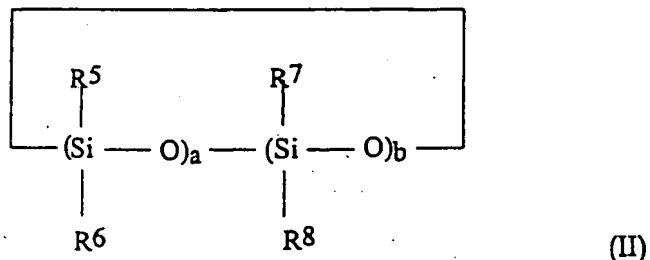
In a preferred embodiment, the linear or branched, volatile siloxane comprises one or more of, hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, dodecamethylpentasiloxane,

tetradecamethylhexasiloxane or hexadecamethylheptasiloxane or methyltris(trimethylsiloxy)silane. In a more highly preferred embodiment, the linear or branched, volatile siloxane of the present invention comprises octamethyltrisiloxane, decamethyltetrasiloxane, or
 5 dodecamethylpentasiloxane or methyltris(trimethylsiloxy)silane. In a highly preferred embodiment, the siloxane component of the composition of the present invention consists essentially of decamethyltetrasiloxane.

Suitable linear or branched volatile siloxanes are made by known methods, such as, for example, hydrolysis and condensation of one or more of
 10 tetrachlorosilane, methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, or by isolation of the desired fraction of an equilibrate mixture of hexamethyldisiloxane and octamethylcyclotetrasiloxane or the like and are commercially available.

Compounds suitable as the cyclic siloxane component of the present
 15 invention are those containing a polysiloxane ring structure that includes from 2 to 20 silicon atoms in the ring. Preferably, the linear, volatile siloxanes and cyclic siloxanes are relatively volatile materials, having, for example, a boiling point of below about 300°C at a pressure of 760 millimeters of mercury ("mm Hg").

20 In a preferred embodiment, the cyclic siloxane component comprises one or more compounds of the structural formula (II):



wherein:

R^5 , R^6 , R^7 and R^8 are each independently a monovalent hydrocarbon group;
and

a and b are each integers wherein $0 \leq a \leq 10$ and $0 \leq b \leq 10$, provided that $3 \leq$
5 $(a + b) \leq 10$.

In a preferred embodiment, the cyclic siloxane comprises one or more
of, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane,
dodecamethylcyclohexasiloxane, tetradecamethylcycloheptasiloxane. In a
more highly preferred embodiment, the cyclic siloxane of the present
10 invention comprises octamethylcyclotetrasiloxane or
decamethylcyclopentasiloxane. In a highly preferred embodiment, the cyclic
siloxane component of the composition of the present invention consists
essentially of decamethylcyclopentasiloxane.

Suitable cyclic siloxanes are made by known methods, such as, for
15 example, hydrolysis and condensation of dimethyldichlorosilane and are
commercially available.

It is believed that those dry cleaning solvents useful in the present
invention that lack a cyclic siloxane component would be more stable than
those which include a cyclic siloxane component, in that cyclic siloxanes are
20 known to ring open and polymerize under acidic and basic conditions.

In a first embodiment of the method of the present invention,
approximately 100 parts by weight ("pbw") of siloxane solvent that may
contain up to 0.1, preferably up to 0.01, even more preferably up to 0.001 pbw
of an acidic impurity is contacted with up to 1000, more preferably up to 500,
25 even more preferably up to 100 pbw of an aqueous solution for about 0.0025
to about 6 hours, more preferably from about 0.001 to about 1 hours, even

more preferably from about 0.01 to about 5 hours, at a temperature of from about 10 to 80°C, more preferably from about 20 to about 60°C. After the siloxane solvent has contacted the aqueous solution for the appropriate time, the mixture of the siloxane solvent and aqueous solution is allowed to settle
5 to form layers, and the aqueous solution is removed by separation, or optionally, separation and drying with an appropriate drying agent.

After removal of the acidic impurities, the solvent can be recycled in the dry cleaning apparatus. The method of the present invention effectively reduces the level of impurities, preferably acidic impurities, in the silicone
10 solvent.

In a second embodiment of the method of the present invention, a dry cleaning fluid is treated by the method of the present invention.

The method of the present invention also comprises a dry cleaning process comprising the steps of: contacting an article with a silicone solvent, and removing the silicone solvent, then treating the silicone solvent that has
15 been removed with an aqueous solution, agitating to ensure good mixing of the solvent and the aqueous solution, and separating the silicone solvent, then reusing the treated silicone solvent in the dry cleaning process. The process of the present invention optionally includes the step of drying the
20 solvent prior to reusing it in the dry cleaning process.

The following examples illustrate the process of the present invention. They are illustrative and the claims are not to be construed as limited to the examples.

EXAMPLES

Decamethylcyclopentasiloxane (D₅) that was used as a dry cleaning solvent was mixed with an acid (LPNC) to make a stock solution containing 200 parts

per million ("ppm") LPNC. Aliquots of the stock solution were heated to 100°C to determine if the mixture would undergo reequilibration and polymerization (increased D₄ and D₆ levels as well as increased viscosity). The results of the control experiments are shown in Table 1 below. Without any added acid, the D₅ was stable at 100°C for 24 hours. In the presence of 200 ppm LPNC, the viscosity rapidly increased over 7 hours and the composition was unable to be determined.

Table 1 - Polymerization and Reequilibration of D₅ with LPNC

Exp #	Temp (°C)	LPNC (ppm)	Rxn Time (h)	% D ₄	% D ₅	% D ₆	Rxn Time (h)	% D ₄	% D ₅	% D ₆	Visc. Increase
Control	100	None	0	<0.2	99.46	0.47	24	<0.2	99.46	0.47	No
1	100	200	7	-	-	-	24	-	-	-	Gel*

*Viscosity was too high to measure.

The acid impurities may be rendered inactive by removing them from the siloxane solvent via liquid-liquid extraction. To remove the acidic impurities, the siloxane solvent (either a linear (MD₂M) or cyclic (D₅) siloxane) containing 1000 ppm of dodecylbenzenesulfonic acid (DDBSA) was contacted with water for 1 minute. The layers were allowed to separate, and the water was removed by separation. In some of the examples, the solvent was also dried with a drying agent. The solution was heated to 100°C for 4 hours and cyclic levels were measured. Heat was then continued until 24 hours, and cyclic levels were again measured. Tables 2 and 3 shows the results of cyclic formation.

Table 2 - Extraction of 1000 ppm acid (DDBSA) from D₅ with 1 min contact time

Exp. #	Dry Yes/No	Rxn time (h)	% D ₄	% D ₅	% D ₆	Rxn time (h)	% D ₄	% D ₅	% D ₆
40	Yes	4	<0.1	99.52	0.48	24	6.5	93.08	0.4
41	No	4	4.39	93.65	1.96	24	2.1	95.84	2.06

Table 3 - Extraction of 1000 ppm acid (DDBSA) from MD₂M with 1 min contact time

Exp. #	Dry Yes/No	Rxn time (h)	% MM	% MDM	% MD ₂ M	% MD ₃ M	Rxn time (h)	% MM	% MDM	% MD ₂ M	% MD ₃ M
42	yes	4	0	0	99.9	0	24	0	0	99.9	0
43	no	4	2.35	2.15	92.86	1.48	24	3.28	6.12	82.7	4.13

As shown in Tables 1 and 2, drying the solvents after contact with water produced better results than when used wet (at 1000 ppm).

The acidic impurity readily initiated polymerization and reequilibration of the D₅ as shown by example 1. Contacting the contaminated silicone solvent with water and then separating the solvent gave a stable silicone mixture that did not polymerize or reequilibrate.

The process of the present invention is effective in reducing the level of acidic impurities in the silicone solvent.

CLAIMS:

1. A method for stabilizing silicone dry cleaning solvents that may contain an undesirable acidic impurity capable of causing cyclic siloxane formation comprising, contacting the silicone dry cleaning solvent with an aqueous solution, and separating the silicone solvent.
- 5 2. The method of claim 1, further comprising agitating to ensure good mixing of the solvent and the aqueous solution.
3. The method of claim 1, wherein the aqueous solution is water, a salt solution, weak base mixture, or combination thereof.
- 10 4. The method of claim 1, wherein the aqueous solution used is up to 1000 parts by weight per 100 parts by weight of silicone solvent.
5. The method of claim 1, wherein the contact time with the adsorbent is from about 0.0025 to about 6 hours.
6. The method of claim 1, wherein the temperature is from about 10°C to about 80°C.
- 15 7. The method of claim 3, wherein the aqueous solution used is selected from the group consisting of water, sodium chloride, potassium chloride, sodium bromide, magnesium sulfate, sodium carbonate and sodium bicarbonate.
8. The method of claim 7, wherein the aqueous solution is water.
- 20 9. The method of claim 1, further comprising drying the solvent with an adsorbent.

10. The method of claim 9, wherein the adsorbent used is selected from the group consisting of 4A molecular sieves, 13X molecular sieves, magnesium sulfate, calcium chloride and calcium sulfate.

5 11. The method of claim 1, wherein the solvent is a linear or branched siloxane comprising one or more compounds of the structural formula:



wherein:

M is $R^1_3SiO_{1/2}$;

10 D is $R^2_2SiO_{2/2}$;

T is $R^3SiO_{3/2}$;

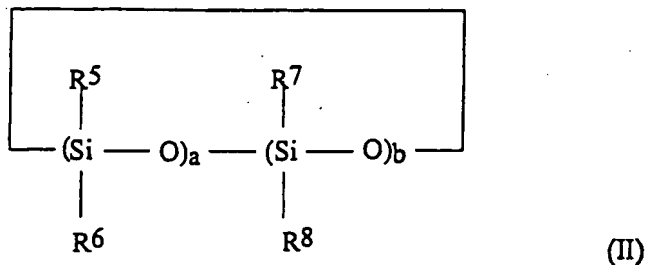
and Q is $SiO_{4/2}$

R^1 , R^2 and R^3 are each independently a monovalent hydrocarbon radical; and

x and y are each integers, wherein $0 \leq x \leq 10$ and $0 \leq y \leq 10$ and $0 \leq z \leq 10$.

15 12. The method of claim 11, wherein the linear or branched, volatile siloxane of the present invention comprises octamethyltrisiloxane, decamethyltetrasiloxane, or dodecamethylpentasiloxane or methyltris(trimethylsiloxy)silane.

13. The method of claim 1, wherein the silicone is a cyclic siloxane comprising one or more compounds of the structural formula:



wherein:

5 R⁵, R⁶, R⁷ and R⁸ are each independently a monovalent hydrocarbon group;
and

a and b are each integers wherein $0 \leq a \leq 10$ and $0 \leq b \leq 10$, provided that $3 \leq (a + b) \leq 10$.

10 14. The method of claim 13, wherein the cyclic siloxane is octamethylcyclotetrasiloxane or decamethylcyclopentasiloxane.

15 15. The method of claim 1, wherein the acidic impurities removed from the solvent are linear phosphonitrilic chloride, sulfuric acid, hydrochloric acid, methanesulfonic acid, dodecylbenzenesulfonic acid, p-toluenesulfonic acid, acetic acid, sulfuric acid or sulfuric acid or a combination thereof.

16. A silicone dry cleaning fluid treated by the method of claim 1.

17. An aqueous solution used in the method of claim 1, wherein the aqueous solution comprises acidic impurities selected from linear phosphonitrilic chloride, sulfuric acid, hydrochloric acid, methanesulfonic acid, dodecylbenzenesulfonic acid, p-toluenesulfonic acid, acetic acid, sulfuric acid and sulfuric acid or a combination thereof.

18. A dry cleaning process comprising:

(a) contacting the article with a silicone solvent; and

(b) removing the silicone solvent; and

(c) contacting the removed silicone solvent with an aqueous solution; and

5 (d) separating the silicone solvent from the adsorbent.

19. The process of claim 18, further comprising agitating to ensure good mixing of the silicone solvent and the aqueous solution.

20. The process of claim 18, wherein the aqueous solution used is selected from the group consisting of water, sodium chloride, potassium
10 chloride, sodium bromide, magnesium sulfate, sodium carbonate and sodium bicarbonate.

21. The process of claim 18, further comprising drying the silicone solvent with an adsorbent before separating the silicone solvent from the aqueous solution.

15 22. The process of claim 18, further comprising reusing the treated silicone solvent in step (1).

23. The process of claim 18, wherein the dry cleaning process comprises a plurality of dry cleaning cycles comprising steps (a) and (b), and a plurality of stabilizing cycles comprising steps (c) and (d), wherein the dry
20 cleaning cycle is repeated one or more times per each stabilizing cycle.

INTERNATIONAL SEARCH REPORT

Int. l. Application No
PCT/US 00/31556

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07F7/20 C08G77/34 D06L1/04 D06L1/02 D06L1/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07F C08G D06L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 016, no. 144 (C-0927), 10 April 1992 (1992-04-10) & JP 04 004224 A (SHIN ETSU CHEM CO LTD), 8 January 1992 (1992-01-08) abstract	1-8, 11-15,17
X	US 5 312 947 A (TSUKUNO AKIHITO ET AL) 17 May 1994 (1994-05-17) column 12; claim 1	1-8, 11-15,17
X	EP 0 277 825 A (TORAY SILICONE CO) 10 August 1988 (1988-08-10) cited in the application column 6; claims 1B,C	1-8, 11-15,17
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/31556

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 543 665 A (SHINETSU CHEMICAL CO) 26 May 1993 (1993-05-26) cited in the application page 8; claim 1	1-8, 11-15,17
X	US 2 834 753 A (GENERAL ELECTRIC COMPANY) 13 May 1958 (1958-05-13) column 13 -column 14; claims 1-3	1-8, 11-15,17
A	US 4 661 612 A (GEORGE ULF ET AL) 28 April 1987 (1987-04-28) cited in the application column 4 -column 6; claims 1-9	1,9,10
A	DE 37 39 711 A (KREUSSLER CHEM FAB) 8 June 1989 (1989-06-08) page 3 -page 4; examples 1-3	1,16,18

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/31556

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 04004224 A	08-01-1992	JP 1989376 C JP 7010919 B	08-11-1995 08-02-1995
US 5312947 A	17-05-1994	JP 2730427 B JP 6107797 A	25-03-1998 19-04-1994
EP 0277825 A	10-08-1988	JP 1647056 C JP 3012073 B JP 63190891 A CA 1316543 A DE 3888372 D DE 3888372 T JP 1742815 C JP 2270885 A JP 4028715 B US 4774346 A	13-03-1992 19-02-1991 08-08-1988 20-04-1993 21-04-1994 06-10-1994 15-03-1993 05-11-1990 15-05-1992 27-09-1988
EP 0543665 A	26-05-1993	JP 2885295 B JP 5140316 A	19-04-1999 08-06-1993
US 2834753 A	13-05-1958	NONE	
US 4661612 A	28-04-1987	DE 3441353 A DE 3508219 A DE 3534218 A DE 3571828 D EP 0186736 A	22-05-1986 11-09-1986 26-03-1987 31-08-1989 09-07-1986
DE 3739711 A	08-06-1989	NONE	